Interface Segregation in Oxide Ceramics: Atomic-Scale Experimental and Theoretical Studies DMR-0303279

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Impurity segregation to ionic grain boundaries has important ramifications for the macroscopic diffusional, mechanical and electrical properties of materials. While some electroceramics such as varistors and positive temperature coefficient of resistance (PTCR) thermistors derive their unique functionalities directly from grain boundary phenomena, most others are at least influenced by local grain boundary behavior.

This NSF-funded research addressed solute segregation in TiO_2 when multiple driving forces for segregation were present. Local grain boundary chemistry was quantitatively determined by analytical transmission electron microscopy and compared to thermodynamic segregation models that incorporated both the electrostatic and elastic strain energy driving forces for solute segregation. In comparison to the experimental results, the theoretical models provided good predictions for several grain boundary parameters including local stoichiometry, solute interfacial excess and space charge layer thickness.

"Grain Boundary Segregation in Yttrium-doped Polycrystalline TiO_2," Qinglei Wang, Guoda D. Lian, and Elizabeth C. Dickey, Acta Materialia, in press.

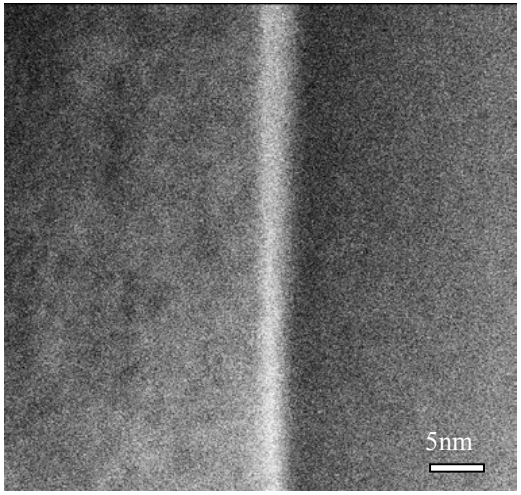

Fig. 1 Z-contrast scanning transmission electron microscopy (STEM) image of a grain boundary in Y-doped TiO_2. The bright intensity at the grain boundary is indicative of the presence of a high atomic number element (Y).

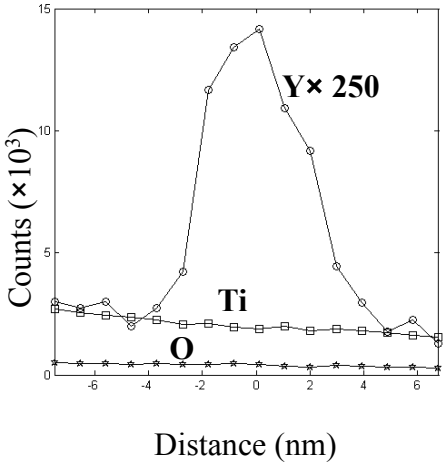

Fig. 2 Chemical profiles across the interface in steps of 1 nm clearly reveal Y segregation to the TiO2 grain boundary. From the data, Y segregation can be quantified and compared to theoretical predictions.

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Schottky and Frenkel defects are the most common defects in the ceramic crystals but the formation mechanism of these defects is not completely understood. It is believed that Schottky defects tend to form in polar ionic crystals with large inter-lattice distances while Frenkel defects tend to preferentially form at highly distorted surfaces and grain boundaries. It has also been suggested that Frenkel defects are just the product of vacancy concentrations that are fixed by the Schottky defect equilibrium.

This NSF-funded research addresses defect formation and diffusion mechanisms in TiO_2 in the bulk, at surfaces, and at grain boundaries. The approach is density functional theory using generalized gradient approximation (GGA) combined with nonlocal, norm-conserving ultrasoft pseudopotential and plane wave expansions. The calculations provide predictions for the formation mechanism of intrinsic defects in TiO_2. Strong anisotropy in interstitial diffusion in rutile TiO_2 is supported by the calculations.

"First Principle Calculations of Intrinsic Defects in Rutile TiO_2 " Jun He, Susan B.Sinnott, and Elizabeth C. Dickey, 50th AVS International Symposium Presentation.

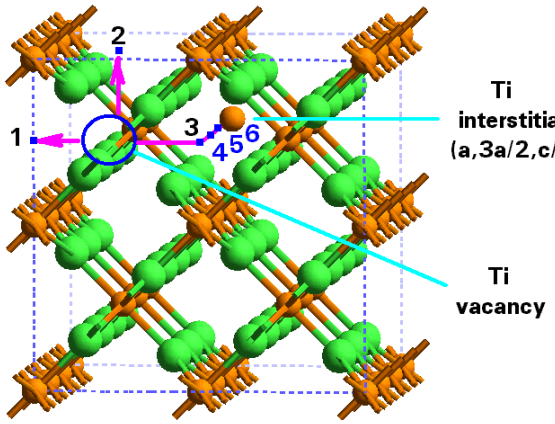

Fig. 1 Frenkel defect model for a 2×2×3 unit cell (9.32Å×9.32Å×8.92 Å) of bulk TiO_2. The Ti interstitial is located at different octahedral sites.

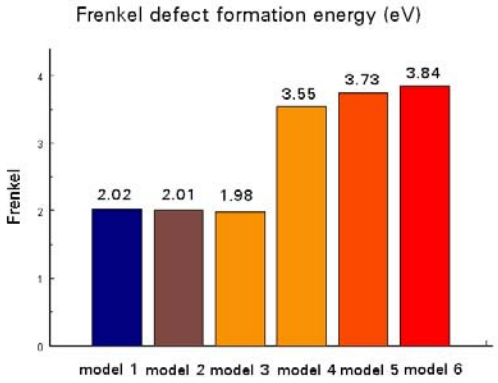

Fig. 2 Defect formation energies for different Frenkel defect models shown in Fig. 1. The lowest Frenkel defect is about 2 eV. This value is lower than the lowest calculated Schottky defect formation energy 3.07 eV. Strong anisotropy in interstitial diffusion in [001] direction in rutile TiO_2 is supported by these calculations.

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Outreach Programs:

- Tyson Bartlett is a high school senior who worked on the construction of heterogeneous metal interfaces and carbon nanostructures for use in first principles, density functional theory calculations. Summer, 2003

- Daphnee Laroche is an undergraduate student who used first principles, density functional theory to calculate defect formation energies in TiO_2. Summer, 2003.